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DESCRIPTION

MATERIAL FOR SLIDING PARTS HAVING SELF-LUBRICITY AND WIRE MATERIAL FOR PISTON RING

TECHNICAL FIELD

The present invention relates to material for use as sliding parts, e.g. piston rings, cylinder liners and vanes, which are incorporated in automotive engines or other internal combustion engines, as well as usual plain bearings, roller bearings, ball bearings, gears and dies.

BACKGROUND ART

Materials having excellent wear resistance property have been applied so far to sliding parts such as cylinder liners and vanes. Materials for piston rings used in internal combustion engines, especially automotive engines, have been changed from cast steel to steel wire, which is processed to ring forms. In usual, the piston rings are produced in such a manner that an ingot with a predetermined composition is hot-worked to wire by forging, hot-rolling or the like, the thus obtained wire is further formed to have a given cross-sectional form corresponding to a small sectional form of a piston ring by drawing or the like, the formed wire is conditioned to have a given hardness, and subsequently the wire is subjected to bending

working so as to be a ring form with a predetermined radius of curvature.

Presently, there are three types of piston ring, which are a top ring, a second ring and an oil ring. These are attached to a piston in the above order from the side of a combustion chamber of an internal combustion engine. Since the top and oil rings are operated under especially severe conditions, employment of steel material has been developed for advanced functionalization in Japan. Such an employment of steel material is a response to demands for further improvement of internal combustion engines in these days. That is, advanced functionalization of internal combustion engines are requested in response to progress of researches on post-internal combustion engines such as electric vehicles. A demand for enhancement of sliding performance has been also intensified in order to deal with diesel engines, which are driven under severe conditions, since diesel engines with a higher internal pressure make an environmental burden smaller than gasoline engines with the provisions that light oil is upgraded and that exhaust gas filters are more functionalized.

By the way, recent researches have been directed also to internal phenomena of engines and elucidated that second rings made of cast steel are subjected to heaviest abrasion among the three piston rings, as reported by the under-mentioned non-patent

literature No. 1.

The other reasons for application of steel material to piston rings in place of cast iron are that in order to employ thin rings, which enables advanced environmental performance of engines, for reduction of a power loss due to a friction force, it is necessary to provide material excellent in mechanical strength and wear resistance property, and that employment of harmless nitriding treatment also accelerates application of steel rings, because of correspondence to severe environmental controls as well as easiness of technology transfer and development of ring-manufacturing process, in place of chrome plating, which has been mainly employed as surface-finishing of cast iron rings.

According to one proposal, a steel piston ring is made resistant to abrasion and seizure by subjecting its surface, which is brought into contact with a cylinder liner, to surface-treatment such as nitriding (see the patent literature No. 1). There has been proposed also another method for improvement of wear resistance property without surface-treatment (see the patent literature No. 2).

*Non-patent literature No. 1: Hideki Saitoh et al. "Researches on abrasion of diesel engines under severe driving conditions", Research report lectures (1999), Kyushu Branch of Japan Society Of Mechanical Engineers (Internet <URL: http://

www.ns.kogakuin.ac.Jp/~ wwa1013/EGR/nagasaki/nagasaki.html>)

*Patent literature No. 1: JP-10-030726 A

*Patent literature No. 2: JP-58-046542 B2

Steel piston rings are outstandingly excellent in mechanical properties and wear resistance property than those of cast iron rings, but have poor seizure resistance property, which is one of reasons that second rings of steel have not been made good progress. Researches for improvement of seizure resistance property are based on reformation of a surface, e.g. nitriding a surface of a steel ring, which comes in contact with a cylinder liner, as reported in the patent literature No. 1. But, such unsolved problems still remain as a cost for surface-treatment and aluminum adhesion which occurs at the interface between a piston and a piston ring.

There has been proposed another method for improvement of seizure resistance property without surface-treatment, as disclosed in the patent literature No. 2, according to which an alloy contains not less than 10% of Cr in order to increase a rate of chromium carbide in a steel matrix. Although an significant improvement in wear resistance property can be attained by such an increase of chromium carbide, there are some concerns in productivity, which include a small improvement in seizure resistance property and deterioration in machinability. As countermeasures

against such disadvantages, the patent literature No. 2 proposes surface-treatments such as PVD, whereas an increase of a manufacturing cost cannot be avoided according to such surface-treatment.

Moreover, in the case of using light oil or even gasoline as fuel, sometimes they contain comparatively much amount sulfur depending upon those quality. When such fuel containing a much amount of sulfur is used in internal combustion engines, piston rings are exposed to a sulfuric dewing atmosphere due to formation of SO_4^{2-} from sulfur contained in the fuel. Therefore, piston rings are also required to be resistant to sulfuric acid corrosion, and thus the requirement to piston rings for improved corrosion resistance property is becoming more strict than it was.

DISCLOSURE OF INVENTION

The present invention is proposed under the above problems, and an object of which is to provide material for sliding parts and wire material for piston rings, wherein the material for sliding parts should be provided with excellent wear resistance property by improving seizure resistance property and nitriding treatment, and wherein the wire material should have excellent property of corrosion resistance to sulfuric acid, excellent productivity and a low friction coefficient.

The inventors have researched and examined sliding motions of sliding parts, which are exposed to a sliding atmosphere in a state of fluid lubrication, represented by environments of piston rings, in detail. As a result, the inventors have discovered an optimum metal structure suitable for improvement of seizure resistance property and a decrease in a friction coefficient as well as a chemical composition suitable for realization of the metal structure resistant to sulfuric acid corrosion.

Thus, according to a first aspect of the invention, there is provided a material for use as self-lubricating sliding parts, which consists of a steel comprising, by mass, from not less than 0.4 % to less than 1.5 % of C (carbon), 0.1 to 3.0 % of Si, 0.1 to 3.0 % of Mn, from inclusive zero to 0.5 % of Cr, 0.05 to 3.0 % of Ni, 0.3 to 2.0 % of Al, 0.3 to 20 % in total (Mo + W + V) of at least one element selected from the group consisting of Mo, W (tungsten) and V (vanadium), and 0.05 to 3.0 % of Cu, wherein there can be observed graphite particles having an average particle size of not more than 3 μm in a section of the metal structure of the steel.

According to one preferable embodiment, the graphite particles observed in a section of the metal structure occupy an area rate of not less than 1 % in the overall area of the structural section, and have an average particle size of not more than 3 μm. More

preferably, no vanadium carbides are observed in the structural section.

Further, preferably the steel contains 0.3 to 5.0 % in total of at least one element selected from the group consisting of Mo and W, and less than 0.1 % V. A preferable Al content is within a range of 0.7 to 2.0 %. Preferably, the steel may further contain 1.5 to 3.0 % of Mo and/or not more than 10 % of Co. Preferably, S (sulfur) and Ca contents of the steel are controlled to be not more than 0.3 % and not more than 0.01 %, respectively. Preferably, the steel is subjected to nitriding treatment to use as sliding parts.

According to a second aspect of the invention, there is provided a wire material for use as piston rings, which consists of a steel comprising, by mass, from not less than 0.4 % to less than 1.5 % of C (carbon), 0.1 to 3.0 % of Si, 0.1 to 3.0 % of Mn, from inclusive zero to 0.5 % of Cr, 0.05 to 3.0 % of Ni, 0.3 to 2.0 % of Al, 0.3 to 20 % in total (Mo + W + V) of at least one element selected from the group consisting of Mo, W (tungsten) and V (vanadium), and 0.05 to 3.0 % of Cu, wherein there can be observed graphite particles having an average particle size of not more than 3 μm in a section of the metal structure of the steel. A piston ring made of the wire material has a metal structure in which sulfide inclusions observed in the structural section, being parallel to the periphery of

the piston ring, are distributed such that straight lines each passing through a major axis of the respective sulfide inclusion cross one another within a cross angle of not more than 30 degrees which angle is referred to as a degree of parallelism. According to one preferable embodiment, the graphite particles observed in a section of the metal structure occupy an area rate of not less than 1 % in the overall area of the structural section, and have an average particle size of not more than 3 μm.

The wire material for use as piston rings preferably contains not more than 10 mass % of Co, and further contains not more than 0.3 mass % of S (sulfur) and not more than 0.01 mass % of Ca. Preferably it is subjected to nitriding treatment to use as piston rings.

A key aspect of the invention is realization of the particular metal structure of steel, in which fine graphite particles are precipitated in a steel matrix by a proper rate, in order to improve seizure resistance property of steeland lower a friction coefficient of sliding parts such as piston rings. Namely, the present invention aims at improvement of durability fully taking peculiar frictional motions between piston rings and cylinders into consideration. According to the invention metal structure, it is possible to attain satisfactory advantageous effects in the above posed subjects which are to improve seizure

resistance property of steel and lower a friction coefficient, and on which the prior art has been unsatisfactory even in connection with non-surface-treatment material or nitrided material which is advantageous in a cost of surface-treatment.

With regard to the invention metal structure with graphite precipitates, the present inventors sought for chemical components which enable fully rapid precipitation of fine graphite particles and also be effective in improvement of workability and machinability of steel in order to establish the metal structure as industrially applicable means. Fruitful results are that further improvement in the above effects could be attained by addition of a single element of sulfur or of sulfur and Ca to the steel. This is another key feature of the present invention.

First, the invention metal structure with graphite precipitates will be described.

A sliding part is mainly designed for fluid lubrication, wherein a fluid film such as oil or water is constantly formed between mechanical elements which are brought into sliding contact with each other under severe conditions. Formation of the fluid film leads to application of buoyancy to a relatively moving fluid, as noted by relative motion of an airplane in the air. The fluid film between sliding parts becomes thicker as viscosity rise of the fluid or an increase of a relative velocity, so that mechanical elements are

protected from abrasion.

However, most of internal combustion engines are the reciprocation type that a relative velocity between a piston ring and a cylinder becomes zero in the vicinity of upper and lower dead points, so that sliding parts suffer often wear and/or seizure due to break of the fluid film, resulting in abnormal motion of internal combustion engines. Furthermore, since inhibition of oil inflow into a combustion chamber, so-called as "oil scraping", becomes an important factor for advanced performance of piston rings, it is difficult to maintain the fluid film in a state suitable for the purpose.

Nevertheless, the inventors have reviewed various fluid lubricating modes during sliding motion for effective use of fluid lubrication in order to overcome the above problems. In short, the fluid lubricating mode comprises three actions, i.e. (1) wedging, (2) expansion/contraction, and (3) squeezing. The squeezing action (3) is effective even in the state that a relative velocity becomes zero. The squeezing action can be explained as follows, on the presumption that a solid plate is sliding on a base plate in presence of a fluid. On such a presumption, distribution of a pressure, which acts on a surface of the solid plate facing to the base plate, is under the boundary condition that a pressure becomes zero at an edge of the solid plate. The pressure distribution

shall be varied according to a domed function in order to generate a positive pressure distribution necessary for maintenance of lubrication. Such pressure distribution is represented by the formula of:

$$\frac{\partial^2}{\partial x^2}P + \frac{\partial^2}{\partial y^2}P < 0 \qquad \text{--- Formula 1}$$

In the formula 1, P is a pressure, x is a sliding direction, and y is a distance along a direction perpendicular to the sliding direction. Reynolds equation, i.e. a principal equation for fluid lubrication, is represented by the formula of:

$$\frac{\partial}{\partial x}\left(\frac{\rho h^3}{12\eta}\frac{\partial P}{\partial x}\right) + \frac{\partial}{\partial y}\left(\frac{\rho h^3}{12\eta}\frac{\partial P}{\partial y}\right) = \frac{u}{2}\frac{\partial(\rho h)}{\partial x} + \frac{\rho h}{2}\frac{\partial u}{\partial x} + \frac{\partial(\rho h)}{\partial t} \qquad \text{--- Formula 2}$$

In Formula 2, ρ is a density of a fluid, h is a thickness of a fluid film, η is a viscosity coefficient, t is a time, and u is a relative velocity. A condition necessary for generation of a positive pressure in the fluid film can be written by Formula 3 according to Formulas 1 and 2.

$$\frac{u}{2}\frac{\partial(\rho h)}{\partial x} + \frac{\rho h}{2}\frac{\partial u}{\partial x} + \frac{\partial(\rho h)}{\partial t} < 0 \qquad \text{--- Formula 3}$$

Formula 3 has three terms. First and second terms, which involve the relative velocity u, correspond to the wedging and the expansion/contraction, respectively, mentioned as the above. The third term, which does not involve the relative velocity u, corresponds to the squeezing

action, which is expected to be effective even under the condition that the relative velocity becomes zero between a piston ring and a cylinder.

The condition that the third term is negative has the physical meaning that a fluid film rapidly decreases in thickness with the provision that the fluid density is constant, resulting in generation of a positive pressure in the fluid film. Such a phenomenon is practically realized by abruptly applying a vertical load to a solid plate, which is sliding on a base plate, so as to squeeze the fluid film. Consequently, a high positive pressure is simultaneously generated by squeezing the fluid film, and the sliding plate hardly comes in direct contact with the base plate. In short, the squeezing action is realized.

The inventors have found that the squeezing action is intensified by reforming a sliding surface to a structure, which includes many fine pores. Fine pores in the sliding surface retain a fluid therein and instantaneously supply the fluid therefrom to a dry surface even under the condition that the fluid film is collapsed at a relative velocity being zero. A significant decrease in thickness of the fluid film, which is originated in movement of the fluid, leads to the squeezing action. As a result, seizure is inhibited in the vicinity of upper and lower dead points during reciprocating motion, and a friction coefficient is also decreased.

The graphite-precipitated structure according to the present invention is determined in order to achieve the above actions and effects. That is, graphite particles not only act as a solid lubricant but also promote formation of oil-retaining pores after dropout thereof. The pores realize the squeezing action suitable for retention of an oil film. The squeezing action, which ensures formation of a stable oil film regardless of pressure fluctuations, is intensified by presence of pores on a sliding surface, as mentioned above. Precipitation of graphite particles is exactly effective for intensification of the squeezing action, and the effectiveness is ensured for normal sliding parts, e.g. sliding bearings, roller bearings or ball bearings and also for sliding parts, e.g. piston rings, cylinder liners, shims of valve lifters, cams, gears, dies or cutting blades, which are difficult to constantly form such a fluid lubricant film due to significant fluctuations of a pressure.

The graphite-precipitated structure is also effective for inhibition of adhesive wear, which have become a problem recently, in the case where it is applied to a piston ring attached to an aluminum piston. Since aluminum is scarcely soluble in carbon, adhesive reaction is suppressed.

The invention material for use as sliding parts has the structure that graphite particles are distributed therein. It is important to control

graphite particles, which are observed in a structural section, to a size of not more than 3 μm in average. If an average size exceeds 3 μm, graphite particles are often damaged at peripheries during sliding motion, and graphite debris unfavorably invade sliding planes. The distribution of graphite particles is more effective under the condition that graphite particles observed in a section of the metal structure occupy an area rate of not less than 1 % in the overall area of the structural section. With regard to relatively large graphite particles of not less than 1 μm, it is more preferable to make the graphite particles to have an average size of not more than 5 μm or an area rate of not more than 5 % in the overall area of the structural section.

Formation of pores, which is effective for lubrication but leads to reduction of a fluid film due to the above function and become ineffective in the end, has not been regarded as an important factor for a fluid lubricating design. However, the invention means is effective especially for internal combustion engines, which involve reciprocating motion with difficulty to continuously form a fluid film. For instance, graphite precipitates become more effective under the condition that irregular frictional behaviors, wherein the temporary state that a fluid film is collapsed in the vicinity of upper and lower dead points at a relative velocity being nearly zero is turned to a state with a plenty of lubricating oil, are

repeated between piston rings and cylinders.

A lubricating design, which enables retention of a fluid film, is important especially under the condition that the fluid film breaks temporarily due to structural reasons, represented by relative motion between piston rings and cylinder liners. Regardless of the lubricating design, possibility of solid contact rises in correspondence with changes in rotating speeds of engines or structures of sliding parts. In this regard, application of material, wherein graphite particles effective for solid lubrication are dispersed, to such irregular sliding parts ensures sufficient lubrication under various sliding conditions.

An alloy design of the invention steel, which is formed to sliding parts, will be understood from the following explanation:

There are reports on graphitic steels from of old, but most of such reports are about Si or Ni-alloyed steels. Besides, it takes several tens hours or longer to hold steels at an elevated temperature of not lower than 600°C for precipitation of graphite particles. According to the present invention, an element Al, which accelerates decomposition of cementite, is alloyed together with Ni at a proper ratio in order to complete precipitation of graphite particles in a several hours.

Since carbon is generally precipitated as

semi-stable cementite in a steel matrix in prior to precipitation of graphite, cementite shall be decomposed and changed to stable graphite in a graphitizing process. Conventional graphitic steels have the disadvantage that cementite is hardly decomposed, so that a fairly long time is required for precipitation of graphite particles. On the other hand, the present invention employs an alloy design, wherein elements such as Cr, which impede decomposition of cementite, are controlled so as to complete decomposition of cementite in a short time, even when semi-stable cementite is precipitated. As a result, carbon is precipitated as graphite at once without substantial formation of cementite.

A diffusion velocity of pores is raised by addition of Al, which has a high diffusion velocity in steel. The higher diffusion velocity accelerates aggregation of pores, which serve as sites for precipitation of graphite particles. Consequently, precipitation of graphite particles is completed in a short time due to the effect of Al and the rapid aggregation of pores. Furthermore, precipitation of graphite particles in a surface layer only is facilitated by nitriding or the like.

Addition of Al is also suitable for an alloy design of a nitriding hardened steel, since Al is a nitriding hardening element. Another element Cr, which has the same nitriding hardening effect, unfavorably

impedes precipitation of graphite particles as a fundamental technological gist of the present invention and also causes significant degradation of corrosion resistance to sulfuric acid. In this sense, addition of Cr is avoided as much as possible, but Al is alloyed as the most important element for the purpose.

Nitriding of graphite steel has been regarded as material inappropriate for precipitation of graphite, since precipitation of graphite particles in the nitriding steel is accompanied with the disadvantage that a nitrided layer is embrittled by presence of graphite particles of not less than 10 μm in size, which act as faults, in the nitrided layer. According to the present invention, the disadvantage is suppressed by reforming graphite precipitates to fine particles.

Reformation of graphite precipitates to fine particles may be achieved by either one of (1) introduction of work strains to divide graphite precipitates, (2) inclusion of Al_2O_3 or the like and (3) dispersion of BN, TiC or the like, which serves as a site for precipitation of graphite. However, the method (1) puts restrictions on manufacturing conditions, and the method (2) needs difficult processing for dispersion of Al_2O_3 or the like. The remaining method (3) also needs difficult processing as for high- carbon steel, since proper dispersion of BN, TiC is achieved only by strict control of trace

components. As for the known reformation, dispersion of TiC is disclosed by JP-11-246940 A, and precipitation of BN as a site for precipitation of graphite is disclosed by Iwamoto et al., "Iron and Steel" vol.84 (1998), p.57. But, any method requires heat-treatment for precipitation of a secondary phase in a high-temperature zone of 1000°C or higher in order to raise a diffusion velocity, so that it is hardly applicable to high-alloy steel, wherein alloying elements are likely to significantly aggregate, due to difficulty in uniform distribution of fine graphite particles.

The inventors have studied precipitation of fine graphite particles from various aspects and discovered that precipitation of a Cu-Al intermetallic compound in a steel matrix is effective for the purpose. The Cu-Al intermetallic compound, i.e. a secondary phase, which serves as a site for precipitation of graphite, is precipitated at a relatively low temperature of not higher than 800°C, so as to enable formation of a stable structure with fine graphite particles in a short time. Since Cu and Al contents are controlled at levels for inhibiting embrittlement according to the present invention, a graphitic structure is formed as a lubricant phase without degradation of mechanical strength. Moreover, the additive Cu is also effective for improvement of corrosion-resistance to sulfuric acid.

Although there are many proposals heretofore on distribution of graphite particles in cast steel for lubrication, material for use as sliding parts has been changed from cast steel to surface-treated steel in response to deterioration of environments, to which various sliding parts are exposed. But, in a case of cylinder blocks, which mostly comprise aluminum parts, cast steel with a graphite-precipitated structure is still used as material for inner walls of cylinder liners aiming at the above effects. A sliding part of the present invention is characterized by the alloy design suitable for employment of steel material, which still has properties of cast steel, in order to impart mechanical strength, wear resistance property and corrosion-resistance to sulfuric acid, which are necessary to cope with deterioration of environments, as well as sliding properties. Chemical components of the sliding part will be understood from the following explanation:

Carbon is an important element, a part of which solution-hardens a steel matrix, another part of which is precipitated as carbides and the remaining of which is precipitated as graphite. Carbide and graphite precipitates improve wear resistance and seizure resistance properties. At least 0.4 mass % of C is necessary for realization of such effects. However, excess carbon of not less than 1.5 mass % unfavorably lowers a melting temperature of the

carbides, so that a metal structure is hardly homogenized by diffusion annealing, e.g. heating an ingot at around 1200°C for several tens hours, for elimination of solidification segregation. In this sense, a carbon content is determined within a range of not less than 0.4 mass % but less than 1.5 mass %, preferably 0.5 mass % or more but less than 1.3 mass %.

Si is added as a conventional deoxidizing agent and also as an accelerator for precipitation of graphite. Si is also effective for improvement of corrosion resistance to sulfuric acid. In this regard, a lower limit of Si is determined at 0.1 mass %. Moreover, the additive Si suppresses softening of steel during annealing, and the effect of Si is important especially in low-alloy steel. A Si content is preferably determined at a value of not less than 1.0 mass % in order to raise high-temperature strength without annealing softening. However, an upper limit of Si is controlled to 3.0 mass %, since excess Si unfavorably raises a A_1 temperature. Therefore, the Si content is determined within a range of 0.1 to 3.0 mass %, preferably 0.5 to 3.0 mass %, more preferably 1.0 to 3.0 mass %.

Mn is added as the same deoxidizing agent as Si. At least 0.1 mass % of Mn is necessary for deoxidation, but excess Mn impedes precipitation of graphite. In this sense, an upper limit of Mn is controlled to 3.0 mass %, and a Mn content is

determined within a range of 0.1 to 3.0 mass %.

Cr is an effective nitriding hardening element, but unfavorably suppresses decomposition of semi-stable cementite and strongly impedes precipitation of graphite. Also Cr significantly deteriorates corrosion resistance property to sulfuric acid. Therefore, an upper limit of Cr content is controlled to 0.5 mass. In this sense, a Cr content is determined within a range of 0 to 0.5 mass %, preferably 0 to 0.3 mass %.

Ni is an accelerator for precipitation of graphite and also effective for inhibition of red shortness, which often occurs in Cu-alloyed steel, but unfavorably raises solubility of carbon in Fe, resulting in poor workability in an annealed state. Therefore, a Ni content is determined within a range of 0.05 to 3.0 mass %, preferably 0.6 to 1.5 mass %.

Al is an element effective for raising nitriding hardness as well as Cr. Since an increase of Cr is necessarily avoided in the invention alloy design, nitriding hardness is ensured at a value suitable for the purpose by addition of Al. The element Al acts as a graphite former, promotes diffusion of pores and also forms a Cu-Al phase, which serves as a site for precipitation of graphite, together with Cu. Namely, Al is an effective element for precipitation of fine graphite particles in a short time, so that an Al content shall be not less than 0.3

mass %. An upper limit of Al is controlled to 2.0 mass %, since an increase of Al raises an A_1 temperature as well as Si. Therefore, an Al content is determined within a range of 0.3 to 2.0 mass %, preferably 0.7 to 2.0 mass %.

Mo is a carbide former, which does not impede precipitation of graphite so much in comparison with Cr but improves heat-resistance of steel. Molybdenum carbide restrains a steel matrix at a thermoforming step, which follows a bending step in a piston ring-manufacturing process, resulting in improvement of dimensional stability. However, excess Mo impedes decomposition of cementite as well as Cr.

Nevertheless, the effect of Mo on impedance of graphitization is weak, but the additive Mo remarkably improves heat-resistance and dimensional stability during heat-treatment. Especially in a piston ring-manufacturing process, which involves heat-treatment of fine wire, the effect of Mo on dimensional stability is important for suppressing deviations of abutment profiles. In this sense, Mo is added at a ratio of 0.3 mass % or more. On the other hand, an upper limit of Mo is controlled to 20 mass %, since precipitation of graphite is impeded as an increase of Mo. V and W have the same effects as Mo. Therefore, at least one element selected from the group consisting of Mo, W and V is added at a ratio within a range of 0.3 to 20 mass % in total.

It is preferable to form a metal structure, wherein vanadium carbide is not observed in a structural section, even in vanadium alloyed steel, since precipitation of graphite is significantly impeded by vanadium carbide. In the case where V is added solely or together with both Mo and W, a ratio of V is preferably controlled to a value less than 0.1 mass % with 0.3 to 5.0 mass % in total of Mo and W. The element Mo intensifies a squeezing action of graphite and promotes formation of a fluid film at a high pressure, resulting in improvement of seizure resistance property and a decrease in a kinetic friction coefficient. Furthermore, sulfuric acid corrosion resistance property is improved by addition of Mo. Therefore, the amount of a single additive Mo is preferably controlled within a range of 1.5 to 3.0 mass %.

Cu is an important element as well as Al, for precipitation of a Cu-Al intermetallic phase and rapid formation of a stable structure with fine graphite particles. The additive Cu is also effective for improvement of sulfuric acid corrosion-resistance. In this sense, it is necessary to control a ratio of Cu in relation with Al, and a Cu content is determined at a value of not less than 0.05 mass %, preferably not less than 0.2 mass % for realizing effects of Cu and the Cu-Al phase. However, excess Cu causes an increase of hardness in an annealed state and degrades workability

of steel, so that an upper limit of Cu is controlled to 3.0 mass %. Therefore, a Cu content is determined within a range of 0.05 to 3.0 mass %, preferably 0.2 to 3.0 mass %.

By the way, sulfur is conventionally added as an organized extreme-pressure additive to engine oil, which is supplied to an internal combustion engine, for improvement of lubrication and inhibition of seizure. The inventors have hit upon inclusion of sulfide MnS in a steel matrix on the contrary. The sulfide serves as a sulfur source for forming an *in situ* sulfide film on a fresh plane, which is exposed by frictional heat, and the sulfide film effectively improves lubricating performance. According to the invention means, excellent lubricating performance is almost permanently ensured due to distribution of the lubricant in the steel material without necessity of adding a plenty of a lubricant for improvement of lubricity at predetermined parts or without disappearance of lubricating performance, which often occurs during exchange of engine oil containing the extreme-pressure additive.

Another conventional means for an increase of chromium carbide in steel for use as a piston ring aims at reduction of a surface area of a piston ring, which comes in contact with a cylinder liner, and enhancement of wear resistance property of the piston ring, to which a sliding energy is applied at a high rate per

unit area, in order to balance abrasion between the piston ring and the cylinder liner. Although seizure resistance property is improved by distribution of chromium carbide, distribution of chromium carbide is directed to prevention of partial bearing from abnormal rising, by such a situation, which is essentially caused by non-uniform contact, as to promote abrasion of the cylinder liner for increase of a contact area. In short, the distribution of chromium carbide makes the piston ring compatible with the cylinder liner at the beginning of attachment, but becomes ineffective on abrasion properties, e.g. adhesive abrasion, with durability.

Excessive improvement of wear resistance property leads to the situation that the cylinder liner is attacked by the piston ring. If the cylinder liner is extremely attacked, a clearance unfavorably becomes larger, resulting in an increase of a blowby rate, which corresponds to a volume of exhaust gas. On the other hand, the additive sulfur has effects on improvement of seizure resistance property due to a decrease in a friction coefficient without accelerated abrasion of the steel material, so that an internal combustion engine is driven for a long while without substantial change of a clearance.

Namely, the invention material for use as sliding parts is further improved in seizure resistance property by addition of sulfur at a proper ratio. The

element sulfur is mostly formed to MnS by reaction with Mn, and the reaction product MnS acts on engine oil as a lubricant to exhibit lubricity. Consequently, a friction coefficient is decreased, and seizure resistance property is improved.

Seizure is the phenomenon that rubbing surfaces are clung together due to transfer of atoms therebetween. The transfer of atoms is promoted by thermal oscillation in the state that the rubbing surfaces are heated at a high temperature due to frictional heat. A temperature of the rubbing surface is represented by a monotonously increasing function in relation with a friction energy, i.e. (a friction coefficient × bearing × a slip velocity. That is, as a decrease in a friction coefficient, a temperature hardly rises, resulting in improvement of seizure resistance property. Addition of sulfur is effective for such a decrease in the friction coefficient, but excess sulfur causes degradation of mechanical properties with the fear that steel wire would be broken down in a drawing step for manufacturing steel piston rings. Therefore, an upper limit of sulfur is controlled to 0.3 mass %. A sulfur content is preferably determined within a range of 0.01 to 0.3 mass %, more preferably 0.03 to 0.3 mass %.

The inventors have also found that an increase of a forging rate, which is applied to material containing up to 0.3 mass % of sulfur in a

manufacturing process, effectively improves mechanical properties of sliding parts. That is, the mechanical properties are upgraded as an increase of the forging rate. Especially when steel piston rings are manufactured by bending steel wire, the increase of a forging rate advantageously prevents the steel wire from fracture and breakage during bending.

The forging rate is defined by a sectional ratio of an ingot to a product profile in a piston ring-manufacturing process. The forging rate is represented by a ratio of (a sectional area of an unforged ingot) / (a sectional area of a bent product), with respect to a section of steel material perpendicular to a forging or drawing direction or a small section of a piston ring as a final product. But, a sectional reduction ratio from steel wire to a piston ring product is negligible small for realization of the above effects, so that the forging rate may be evaluated by a ratio of (a sectional area of an unforged ingot) / (a sectional area of steel wire, which is forged and drawn but unbent). As the forging rate is higher, the material is more heavily forged.

Steel, which distributes sulfide MnS therein, originally has the cast structure that there are many spheroidal or spindled sulfide inclusions with random orientation at triple points of grain boundaries in a cellular solidification structure. Orientation of the sulfide inclusions are gradually changed as an increase

of the forging rate, resulting in improvement of mechanical properties.

As an increase of the forging ratio, sulfide inclusions are more oriented along a longitudinal direction of steel wire and elongated in a state corresponding to a peripheral stress, which is mainly applied to a piston ring. Consequently, unfavorable effects of sulfide inclusions on mechanical properties are substantially eliminated. Degradation of mechanical properties is typically prevented by reforming sulfide inclusions to a shape with an aspect ratio (a major axis size / a minor axis size) of 3 or more. In other words, poor orientation of sulfide inclusions with an aspect ratio of 3 or more along a peripheral direction leads to degradation of mechanical properties.

Concretely, distribution of sulfide inclusions, especially sulfide inclusions with an aspect ratio of 3 or more, which are microscopically observed on a surface structure parallel to a periphery of a piston ring, is controlled to the state that a parallelism (an angle at an acute side) between straight lines, each of which passes through a major axis of a separate sulfide, is held within a range of not more than 30 degrees, in order to provide steel wire useful as piston rings or material useful as sliding parts. In this sense, the forging rate is preferably determined at a value of 500 or more.

Fig. 5 is a set of schematic views, which illustrate microstructures of unforged steel with a forging rate of 1 (as cast) and forged steel with a forging rate of 500 in an unetched state observed by an optical microscope, and schemes for explaining measurement of a parallelism of sulfide inclusions. Two of sulfide inclusions with an aspect ratio of 3 or more are arbitrarily selected, an angle at an acute side between straight lines (a line-A and a line-B), each of which passes through a major axis of a separate sulfide, is measured, and the measurement is repeated over a whole of the microscopic view. The same measurement is further repeated for at least ten microscopic views. A maximum value among the measured angles is evaluated as the parallelism. In the case where there is no intersection (as noted in the forged steel with a forging rate of 500 in Fig. 5), a line-A' parallel to the line-A may be regarded as an auxiliary line. Herein, sulfide, which is observed as a connected particle in a 400 times microscopic view, is regarded as a separate inclusion, and a straight line, which passes through a major axis of the separate inclusion, is determined as a measuring line.

In Fig. 5, the unforged steel with a forging rate of 1 has the structure that sulfide inclusions are distributed with a parallelism more than 30 degrees, but the forged steel with a forging rate of 500 has the structure that any parallelism is controlled to a value

of not more than 30 degrees. In fact, the figure of 30 degrees is a designed value according to rupture mechanics. Fig. 6 is a graph, which illustrates analytical results by G. R. Irwin, "Analysis of Stresses and Strains Near the End of a Crack Transversing a Plate", Trans. ASME, Ser. E, J. Appl. Mech., Vol.24, No. 3 (1957), pp.361-364, for explaining how to change a stress intensity factor in the state that cracks propagate along a direction different from a stress direction. The analytical results are represented by the formula of:

$$K_I = (1-\cos^2 \beta)\cdot \sigma\sqrt{\pi a} \qquad \text{---Formula 4}$$

In Formula 4, K_1 is a a stress intensity factor, β is an angle between a stress direction and a crack-propagating direction, σ is a stress, and a is a length of a crack. Formula 4 indicates that propagation of a crack, which is perpendicular to a stress direction (at β=90 degrees), is facilitated, while a crack, which extends along a stress direction (at β=0), does not propagate so much. Facilitation of propagation (i.e. an abrupt increase of a stress intensify factor) corresponds to an angle of 30 degrees. Since the inclusions can be regarded as cracks due to poor kinetic bonding strength, it is understood that distribution of the inclusion with controlled deviation of orientation within a range of not more than 30 degrees, i.e. orientation arrangement

of elongated inclusions, is important to inhibit propagation of cracks.

Since sulfur is a representative element unfavorable for mechanical properties of steel, proper means for improvement of strength is desired to make steel material applicable to piston rings. For instance, a proposal of JP-07-258792 A, which allows at most 1 mass % of sulfur, principally relates to cast steel, which is formed to a cylinder liner or else with an insufficient forging rate. However, a practical process for manufacturing steel piston rings at a economical cost is achieved by metal forming such as drawing, rolling and bending. If such steel containing up to 1 mass % of sulfur is processed to wire for use as piston rings by the metal forming, the steel may be broken down in a drawing step due to shortage of material strength necessary for the metal forming. As a result, it is difficult to manufacture steel piston rings with high reliability.

According to the present invention as mentioned the above, material, which contains not more than 0.3 mass % of sulfur, is preferable for use as sliding parts in order to further improve seizure resistance property. Controlled addition of sulfur is typically meaningful in wire material, which is formed to a product profile with a high forging rate, for use as piston rings.

The effect of sulfur is more enhanced by

addition of Ca together with sulfur. The element Ca, which has a strong reducing power, is included in MnS, so that Ca is likely to ooze out onto a seized surface. Ooze of Ca inhibits formation of oxides on the seized surface but facilitates formation of lubricious sulfides. However, excess Ca is unfavorable for hot-workability, so that an upper limit of Ca is preferably controlled to 0.01 mass %. A Ca content is preferably determined within a range of 0.0001 to 0.01 mass %, more preferably 0.0005 to 0.01 mass %, for achievement of the above effects.

Addition both of sulfur and Ca is also effective for improvement of machinability and grindability other than seizure resistance property. Especially, distribution of MnS and precipitation of graphite particles improve machinability of steel. Due to the improved machinability, a corner of steel material is machined to an objective profile with a small radius of curvature, so that piston rings with a high oil-scraping power can be manufactured with ease.

The invention material for use as sliding parts and piston rings may contain Co for improvement of corrosion-resistance, especially sulfuric acid corrosion-resistance. The element Co as well as Mo intensifies a squeezing effect of graphite and promotes formation of a fluid film at a high pressure, resulting in improvement of seizure resistance property and a decrease in a kinetic friction coefficient. Such

effects of Co are noted at a ratio of not less than 0.5 mass %. But Co is an expensive element, and further improvement is not expected by excess Co. Therefore, a Co content is preferably controlled to not more than 10 mass %, more preferably within a range of 2 to 5 mass %.

The invention steel material for use as sliding parts and piston rings contains the above elements at specified ratios and the balance being substantially Fe. Other elements are controlled to not more than 10 mass %, preferably not more than 5 mass %, in total.

The invention steel material may further contain one or more of the following elements within specified ranges of:

$P \leq 0.1$ mass %, $Mg \leq 0.01$ mass %, $B \leq 0.01$ mass %, $Zr \leq 0.1$ mass %,

A preferable condition of the present invention is to make the metal structure to contain nonmetallic inclusions occupying an area rate of not more than 2.0 % in the overall area of the structural section, whereby preventing fracture in a drawing process during forming steel material to wire and occurrence of breakage during forming the wire to a coil. The specified structure is typically suitable for a piston ring-manufacturing process accompanied with forming and processing fine wire, in order to establish a manufacturing process with high

productivity.

Nitriding further improves seizure resistance and wear resistance properties, as an additional effect in the present invention. Nitriding may be combined with other surface treatment such as PVD or Cr-plating, since excellent seizure resistance property is imparted to steel material regardless of surface-treatment. Take a piston ring as an example. Such surface-treatment is conventionally applied to a main sliding surface of the piston ring, which comes in contact with a cylinder liner, but un-applicable to its friction surface, which cmes in contact with a piston. In short, inhibition of adhesive abrasion can not be expected by the conventional surface-treatment. However, the invention material, which has excellent seizure resistance property and resists to adhesive reaction without necessity of surface-treatment, is extremely useful as piston rings.

The invention material may be subjected to intercalation processing, whereby foreign molecules or ions are inserted into a laminar molecular structure of graphite for further improvement of sliding characteristics by immersion in a $CuCl_2$ solution for instance, due to its metal structure with a graphite phase. Moreover, graphite particles in the intercalation-processed state act as a polymerization catalyst. Therefore, the material is reformed to a state suitable for polymerization of a lubricating oil

by a polymer coat (coating with a polymer film) or intercalation-processing as pre-treatment, in order to provide sliding parts, which maintain self-lubricity originated in polymerizing reaction during sliding motion.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a microphotograph illustrating distribution of graphite particles, which are observed on a section of the invention material (Specimen No. 3);

Fig. 2 is another microphotograph illustrating distribution of graphite particles, which are observed on a different section of the same material as the material of Fig. 1;

Fig. 3 is a microphotograph illustrating distribution of graphite particles, which are observed on a section of a comparative material (Specimen No. 14);

Fig. 4 is another microphotograph illustrating distribution of graphite particles, which are observed on a different section of the same material as the material of Fig. 3;

Fig. 5 is a set of schematic views of microstructures for explaining parallelism of sulfide inclusions;

Fig. 6 is a graph for explaining an effect of an angle between a stress direction and a crack-

propagating direction on a stress intensify coefficient;

Fig. 7 is a schematic view for explaining a frictional abrasion test at a super-high pressure;

Fig. 8 is a schematic view for explaining a reciprocating abrasion test; and

Fig. 9 is Stribeck's diagram illustrating a relationship between a reciprocal number of a load and a kinetic friction coefficient for explanation of lubrication.

EMBODIMENTS

The other features of the present invention will be clearly understood from the following examples.

EXAMPLE 1

Several steels were melted in a high-frequency induction furnace in the open air, adjusted to chemical compositions in Table 1, and cast to ingots of 220 mm × 220 mm in section size. In Table 1, Specimen No. 1 to 6 satisfy definitions of the present invention. Specimen No. 11 to 16 are comparative steels, wherein Specimen No. 16 corresponds to JIS SUS440B, used for conventional piston rings.

Table 1

Specimen No.	Chemical compositions (mass %)															
	C	Si	Mn	Cr	Al	S	Mo	W	V	Mo+W	Mo+W+V	Ca	Ni	Cu	Co	Fe
1	0.42	1.85	2.83	0.25	0.31	0.29	0.5	<0.01	<0.01	0.5	0.5	0.0002	2.96	0.1	<0.01	bal.
2	0.66	0.93	1.21	0.45	0.78	0.13	2.0	2.9	1.2	4.9	6.1	0.0010	0.2	2.8	<0.01	bal.
3	0.79	1.52	1.98	0.31	1.48	0.06	7.2	5.1	<0.01	12.3	12.3	0.0030	0.3	1.1	<0.01	bal.
4	0.98	2.32	1.03	0.21	1.03	0.12	7.5	10.0	0.5	17.5	18.0	0.0060	0.5	1.3	<0.01	bal.
5	1.42	2.78	1.01	0.01	1.91	0.03	2.9	3.0	<0.01	7.9	7.9	0.0098	2.1	0.8	<0.01	bal.
6	0.88	1.55	1.05	0.03	1.03	<0.01	1.05	<0.01	<0.01	1.05	1.1	<0.0001	0.8	0.8	<0.01	bal.
11	0.55	1.49	0.71	0.21	<0.01	<0.01	1.0	2.0	<0.01	3.0	3.0	0.0003	<0.05	<0.05	<0.01	bal.
12	1.00	0.25	0.31	1.48	1.53	<0.01	1.8	3.4	<0.01	5.2	5.2	<0.0001	<0.05	<0.05	<0.01	bal.
13	0.55	1.51	0.72	1.01	<0.01	0.35	4.8	9.9	<0.01	14.7	14.7	0.0002	<0.05	0.8	<0.01	bal.
14	0.78	1.23	0.46	0.03	1.34	0.06	4.2	2.1	<0.01	6.3	6.3	0.0050	2.53	<0.05	<0.01	bal.
15	0.55	1.35	0.55	0.60	<0.01	0.31	0.9	0.9	<0.01	1.8	1.8	<0.0001	1.44	<0.05	<0.01	bal.
16	0.80	0.31	0.40	17.5	<0.01	<0.01	1.0	<0.01	<0.01	1.0	1.0	<0.0001	<0.05	<0.05	<0.01	bal.

Each ingot was hot-worked to wire material of 9 mm × 9 mm in section size at a forging rate of approximately 598, except Specimen No. 13. Specimen No. 13 was forged but was not formed to a test piece due to fracture during hot-working in succession to forging.

The wire material was annealed and then subjected to quench and tempering under predetermined conditions so as to moderate its hardness to around 45HRC. A surface structure of the quenched and tempered wire material was observed in an unetched state by an optical microscope for measuring distribution of graphite particles, i.e. an average particle size and an area rate of graphite particles, which shared the surface structure. The distribution of graphite particles was investigated by image analysis of ten views, which were observed by a 1000 times optical microscope. A size of a graphite particle was represented by a diameter of a real circle, which had the same area as an inspected graphite particle. Specimen No. 1 to 6 had the structure that graphite particles of 0.3 to 2 μm in average size were distributed with the area rate of 0.5 to 5 %.

Figs. 1 to 4 are microphotographs illustrating distribution of graphite particles in Specimen No. 3 and 14. Precipitation of fine graphite particles is detected in a matrix of Specimen No. 3,

but graphite particles in a matrix of Specimen No. 14 are coarse. The difference in particle size between Specimen No. 3 and 14 is explained as follows: Since Specimen No. 4 contains Cu and Al at proper ratios, fine Cu-Al intermetallic particles precipitate in prior to precipitation of graphite and act as sites for precipitation of graphite, resulting in fine graphite particles. On the other hand, the Cu-Al intermetallic phase is ineffective in Specimen No. 14 due to shortage of Cu or Al, so as to allow growth of graphite to coarse particles. Table 2 shows distribution of graphite particles in all the Specimens including Specimen No. 3 and 14. Distribution of graphite particles was not detected in any matrix of Specimen No. 11, 12, 15 and 16.

Each specimen was ion-nitrided 5 hours at 530°C in an atmosphere of $H_2:N_2 = 1:1$ and used as a test piece for evaluation of seizure resistance and wear resistance properties. Seizure resistance property was evaluated by a frictional abrasion test at a superhigh pressure, using a frictional abrasion tester shown in Fig. 7 under the following conditions. A rotating torque of an opposite part, which was held in abrasive contact with the test piece, was measured. A time, at which the rotating torque abruptly rose, was regarded as initiation of seizure, and a load at the time was evaluated as a scuffing load. A kinetic friction coefficient was calculated from a rotating torque of

the opposite part at a load of 10 MPa. In Fig. 7, the numeral 1 is a test piece, the numeral 2 is an opposite part, and the mark F is a load, respectively.

A profile of a sliding surface: a square of 5 mm × 5 mm in size

A friction velocity: 2 m/second

A pressure applied to a friction surface: an initial pressure of 1.5 MPa an increase rate of 0.5 MPa/minute

A lubricant oil: motor oil #30

The lubricating oil was dropped at a rate of 10 cm^3/minute only at an initial stage but stopped thereafter.

An opposite part: JIS FC250 (grey cast iron with hardness of 100 HRB)

Wear resistance property was evaluated by a reciprocating abrasion test, wherein a test piece of 8 mm in diameter and 20 mm in length was rubbed with an opposite part (FC250) of 20 mm in diameter by reciprocating motion for measuring a wearout width of the test piece. A reciprocating abrasion tester is schematically illustrated in Fig. 8, while the other abrasion conditions are under-mentioned. In Fig. 8, the numeral 1 is a test piece, the numeral 2 is an

opposite part, the mark F is a load, and the mark OIL is a lubricating oil, respectively.

A pressing load:	500 N
A sliding distance per cycle:	130 mm
A maximum sliding velocity:	0.5 m/second
A lubricating oil (dropped):	motor oil #30
An opposite part:	JIS FC250 (grey cast iron with hardness of 100 HRB)

Table 2 shows measurement results of scuffing loads, kinetic friction coefficients and wearout widths together with hardness of nitrided layers.

Table 2

Specimen No.	Distributon of graphite		Vanadium carbide	Hardness of nitrided layer (HV)	Scuffing load (MPa)	Kinetic friction coefficient	Width of wearout (mm)	Note
	Average particle size (μm)	Area rate (%)						
1	0.4	0.8	no	853	12.5	0.11	0.55	Inventive examples
2	0.5	0.9	yes	890	11.5	0.12	0.65	
3	0.8	3.5	No	930	10.5	0.07	0.5	
4	0.7	2.6	No	910	13.5	0.08	0.55	
5	1.9	4.1	No	950	10.5	0.07	0.51	
6	0.7	1.9	No	895	12.6	0.06	0.51	
11	undetected	0	No	445	6.5	undetected	1.53	Comparative examples
12	undetected	0	No	773	7.0	undetected	0.71	
14	6.2	5.8	No	723	6.0	undetected	0.64	
15	undetected	0	No	563	7.0	undetected	1.62	
16	undetected	0	No	1032	7.5	undetected	0.53	

Results in Table 2 prove that all the Specimen No. 1 to 6, which satisfy the definitions of the present invention, are excellent in seizure resistance and wear resistance properties due to high scuffing loads and small widths of wearout. Especially, Specimen No. 3 to 6 have small kinetic friction coefficients and properties suitable for use as sliding parts. On the other hand, all the comparative Specimens, which do not satisfy the specified distribution of graphite particles in the present invention, are inferior in seizure resistance property. Poor wear resistance property of Specimen Nos. 11 or 15 is caused by insufficient nitriding hardness due to shortage of Cr and Al as nitriding hardening elements.

Specimens of Example 1, without nitriding treatment, were subjected to a seizure test under the same condition as the above. Results are shown in Table 3. Specimen No. 1 to 6, which satisfy the specified distribution of graphite particles in the present invention, have excellent seizure resistance property without necessity of surface treatment. On the other hand, the comparative Specimen No. 14 has a smaller scuffing load. When a sliding surface of the Specimen No. 14 was microscopically observed after the seizure test, fracture of graphite particles at peripheries were detected. The observation result suggests invasion of graphite debris into the sliding

surface, resulting in degradation of sliding characteristics.

Table 3

Specimen No.	Distribution of graphite		Scuffing load (MPa)	Note
	Average particle size (μm)	Area rate (%)		
1	0.4	0.8	11.5	Invention Specimen
2	0.5	0.9	10.5	
3	0.8	3.5	11.0	
4	0.7	2.6	13.0	
5	1.9	4.1	12.0	
6	0.7	1.9	11.5	
11	Undetected	0	6.5	Comparative Specimen
14	6.2	5.8	6.0	

EXAMPLE 2

Each of Specimen No. 1 and 15 in Table 1 was hot-rolled to a coil of 5.5 mm in diameter and then processed to a flat wire profile of 1.5 mm × 3.1 mm in section size by drawing and cold-rolling. Specimen No. 1 was formed to the objective profile without troubles, but Specimen No. 15 was broken in a drawing step due to its poor cold-workability. A metal structure of each billet of Specimen No. 1 and 15 was microscopically observed in an undrawn state along a direction perpendicular to a rolling direction and analyzed for measuring the area rate of nonmetallic inclusions. The area rate of nonmetallic inclusions was 1.86 % in

Specimen No. 1, but 2.23 % in Specimen No. 15. Comparison of the observation results indicates that breakage of Specimen No. 15 was caused by excess nonmetallic inclusions at a ratio above 2.0 % in addition to excess sulfur.

EXAMPLE 3

Each of Specimen No. 1 to 6, 11 and 12 was processed to a flat wire profile of 1.5 mm × 3.1 mm in section size under the same condition as Example 2, heated 30 minutes at 1000°C, quenched and tempered to hardness of around 510 HV. The processed test piece was machined 10 times by a grinding cutter at a rotational frequency of 10000 r.p.m and a feed rate of 1 mm/second, for investigating occurrence frequency of burrs. Table 4 shows test results on the occurrence frequency of burrs.

Table 4

Specimen No.	Occurrence frequency of burrs	Note
1	0	Invention specimens
2	0	
3	0	
4	0	
5	0	
6	7	
11	8	Comparative specimens
12	10	

Occurrence of burrs was detected in any of Specimen No. 11 and 12, but no burrs occurred in any of Specimen No. 1-5, to which S was added at a proper ratio. The results prove that addition of S has remarkable effects on suppression of burrs. Consequently, piston rings can be manufactured with high productivity.

EXAMPLE 4

An ingot, which had the same chemical composition as Specimen No. 1 in Table 1, was separately prepared. The ingot was hot-worked to wire of 3.0 mm × 3.0 mm in section size with a forging rate, which was varied within a range of 1 to 10,000. The hot-worked wire was conditioned to hardness of 400 HV by quench and tempering. A parallelism of sulfide inclusions (with an aspect ratio of 3 or more) in a surface structure, which was parallel to an lengthwise direction of the elongated wire and served as a periphery of a piston ring, was measured according to the above-mentioned procedures.

The hardness-conditioned wire material was subjected to a three-point flexure test with a span of 30 mm. A test piece, which was bent with a deflection up to 10 mm without breakage, was evaluated as the mark A, while a broken test piece was evaluated as the mark B. The test results are meaningful for judging feasibility whether quenched and tempered wire material

is formed to a piston ring with a predetermined curvature by roller bending or not. Table 5 shows the test results.

Table 5

Specimen No.	Forging rate	Parallelism (degrees)	Evaluation of breakage
1-1	1	84.5	B
1-2	10	45.2	B
1-3	500	27.8	A
1-4	2000	11.5	A
1-5	10000	3.5	A

It is understood from the results in Table 5 that the metal structure, wherein sulfide inclusions are distributed with a parallelism of not more than 30 degrees, is excellent in mechanical properties and effective for suppression of breakage during bending wire material to a ring profile. The parallelism and the aspect ratio of sulfide inclusions, which were observed on a surface structure parallel to a periphery of a piston ring, were not substantially changed between the wire material and a piston ring, which was manufactured by bending the wire material.

The parallelism of sulfide inclusions, which are observed on a surface structure of wire material, reflects a structure of a piston ring, which is manufactured from the wire material by bending.

Distribution of sulfide inclusions with a parallelism of not more than 30 degrees is effective for improvement of mechanical properties of piston rings, without fears of fatigue fractures, which often occur in conventional engines. In this sense, the specified control of the parallelism is especially suitable for wire material for use as piston rings.

EXAMPLE 5

Several steels were melted in a high-frequency induction furnace in the open air, adjusted to chemical compositions in Table 6 and cast to ingots of 220 mm × 220 mm in section size. Specimen No. 22 contained Mo at a relatively higher ratio, and Specimen No. 23 contained Co at a relatively higher ratio, as compared with Specimen No. 21.

Table 6

W, V < 0.01 mass %, Ca < 0.0001 mass %

Specimen No	Chemical compositions (mass %)											
	C	Si	Mn	P	S	Ni	Cr	Mo	Co	Cu	Al	Fe
21	0.86	1.75	0.30	0.008	0.020	0.30	0.001	0.98	0.01	0.82	1.22	Bal.
22	0.86	1.69	0.30	0.010	0.022	0.30	0.001	1.97	0.01	0.76	1.20	Bal.
23	0.86	1.68	0.31	0.008	0.022	0.31	0.001	0.99	3.99	0.87	1.18	Bal.

Each ingot was hot-worked to wire material of 9 mm × 9 mm in section size with a forging rate of

approximately 598. The wire material was annealed and then conditioned to hardness of around 40 HRC by quench and tempering. Thereafter, a surface structure of the quenched and tempered wire material was observed in an unetched state for measuring distribution of graphite particles (an average size of graphite particles and the area rate of graphite particles, which shared the surface structure). The distribution of graphite particles was investigated by analyzing 10 images, which were observed by a 1000 times optical microscope.

Table 7

Specimen No.	Average size of graphite particles (μm)	Area rate of graphite Particles in the overall area of the structural section (%)	Area rate of graphite particles of 1 μm or more in size in the overall area of the structural section (%)	Average size of graphite particles of 1 μm or more (μm)
21	0.55	1.69	0.41	1.15
22	0.50	2.05	0.14	1.20
23	0.75	3.50	0.70	1.33

Any of Specimen No. 21-23 had a structure with fine graphite precipitates. Graphite particles of not more than 1 μm in size were distributed the area rate of 1 to 4 %, as noted in Table 7. Relatively large graphite particles of 1 μm or more had an average particle size within a range of 1 to 1.5 μm and the area rate of less than 1 % in any of Specimen No. 21 to 23. Namely, it is understood that most of graphite precipitates are fine particles, and an the area rate of the relatively large graphite particles to all the graphite particles was controlled to a value less than 1/4.

Each specimen was used as a test piece for evaluation of a kinetic friction coefficient. Evaluation of a kinetic friction coefficient was performed, using the same frictional abrasion tester shown in Fig. 7 (except friction velocity) under the under-mentioned conditions. A kinetic friction coefficient was calculated from a torque and a load applied to an opposite part, at every moment when a load rose step by steP. Fig. 9 shows a relationship between a reciprocal value of a load and a kinetic friction coefficient.

A profile of a sliding surface:	a square of 5 mm × 5 mm
A friction velocity:	1 m/second
A pressure onto a friction surface:	1.5 MPa at an initial

	stage but raised at a rate of 0.5 MPa/minute
A lubricating oil:	motor oil #30 continuously dropped at a rate of 10 cm^3/minute
An opposite part:	JIS FC250 (grey cast iron)

Fig. 9 is a diagram, so-called as "Stribeck's diagram", for representing conditions of a load, which is applied to a frictionally sliding part, in relation between by load characteristics (abscissa) and a friction coefficient (ordinate). Lubricating situations can be evaluated by the diagram. In a case of the invention examples, the abscissa axis is represented by a reciprocal value of a load, since a friction velocity is kept at a constant value of 1 m/second. In each curve of Fig. 9, the side (a low-stress side, i.e. a range indicated by the arrow) rightward from a plot (an extreme value), where a friction coefficient is smallest, corresponds to a region where fluid lubrication is achieved without damage of a lubricating film. The left side (a heavy-stress side) corresponds to a region where both of fluid and solid lubrications occur due to direct contact of solid parts together. The relation in Fig. 9 indicates that fluid lubrication can be more achieved without damage of a fluid film even under a heavy stress, as a plot (an extreme value), where a friction

coefficient is smallest, shifts leftwards in the diagram.

It is understood from the results in Fig. 9 that Specimen No. 22, which contains Mo at a larger ratio than Specimen No. 21, maintains a fluid film under a heavier load, and that Specimen No. 23, which contains Co at a larger ratio than Specimen No. 21, still maintains a fluid film under a further heavier load. The improved retention of the fluid film proves the effects of Mo and Co, i.e. the above-mentioned squeezing effects.

A plot at the left end of each curve corresponds to a load, when the frictional abrasion test was stopped due to occurrence of seizure. The leftist plots of Specimen No. 22 and 23 shifted leftwards (toward a heavier-stress side) due to addition of Mo and Co in comparison with Specimen No. 21, resulting in further improvement of seizure resistance property. Moreover, the kinetic friction coefficients are decreased as a whole. In short, the effects of graphite precipitates on sliding characteristics are further intensified by addition of Mo and/or Co.

According to the present invention, steel material excellent in seizure resistance property with a small friction coefficient is bestowed with self-lubricity without necessity of surface-treatment, so that the steel material is applicable to various

sliding parts with less energy loss caused by friction. Moreover, the steel material is processed to piston rings, which are less aggressive to cylinder liners and pistons, due to simultaneously controlled distribution of sulfide inclusions. Consequently, the present invention contributes to remarkable improvements of internal combustion engines in environmental ability and durability. Furthermore, the steel material is processed to sliding parts or piston rings at a saved manufacturing cost in a short lead time due to its excellent workability and machinability. Namely, the present invention, which provides material for use as sliding parts excellent from aspects both of performance and processing, is a truly profitable technology in an industrial point of view.

INDUSTRIAL APPLICABILITY

The material proposed by the present invention is useful as sliding parts, such as piston rings, cylinder liners or vanes, which are built in internal combustion engines of automotive engines or the like, as well as sliding bearings, roller bearings, ball bearings, gears and dies.